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Tracing the fate of phosphorus fertilizer derived cadmium in soil-fertilizer-wheat systems using enriched stable isotope labeling☆

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ABSTRACT

Applying mineral phosphorus (P) fertilizers introduces a considerable input of the toxic heavy metal cadmium (Cd) into arable soils. This study investigates the fate of P fertilizer derived Cd (Cd_{dff}) in soil-wheat systems using a novel combination of enriched stable Cd isotope mass balances, sequential extractions, and Bayesian isotope mixing models. We applied an enriched ^{111}Cd labeled mineral P fertilizer to arable soils from two long-term field trials with distinct soil properties (a strongly acidic pH and a neutral pH) and distinct past mineral P fertilizer application rates. We then cultivated wheat in a pot trial on these two soils. In the neutral soil, Cd concentrations in the soil and the wheat increased with increasing past mineral P fertilizer application rates. This was not the case in the strongly acidic soil. Less than 2.3% of freshly applied Cd_{dff} was taken up by the whole wheat plant. Most of the Cd_{dff} remained in the soil and was predominantly (>95% of freshly applied Cd_{dff}) partitioned into the easily mobilizable acetic acid soluble fraction (F1) and the potentially mobile reducible fraction (F2). Soil pH was the determining factor for the partitioning of Cd_{dff} into F1, as revealed through a recovery of about 40% of freshly applied Cd_{dff} in F1 in the neutral pH soil compared with about 60% in the strongly acidic soil. Isotope mixing models showed that F1 was the predominant source of Cd for wheat on both soils and that it contributed to over 80% of the Cd that was taken up by wheat. By tracing the fate of Cd_{dff} in entire soil-plant systems using different isotope source tracing approaches, we show that the majority of Cd_{dff} remains mobilizable and is potentially plant available in the subsequent crop cycle.

1. Introduction

Cadmium (Cd) is a heavy metal that is ubiquitous in the environment and highly toxic, with reported effects on humans, including on the kidney and skeletal, respiratory and reproductive systems (Godt et al., 2006; Järup and Åkesson, 2009; WHO, 2010). Cd can be transferred from soils to plants and enter the human food chain (Kabata-Pendias, 2004; McLaughlin et al., 2020). In Europe, cereals are among the main sources of Cd exposure for the general population (EFSA, 2012). Aside from its natural presence originating from bedrock weathering, Cd mainly enters agricultural soils through atmospheric deposition and through the application of fertilizers that contain Cd impurities (Nziguheba and Smolders, 2008; Six and Smolders, 2014). Among the latter, phosphorus fertilizers derived from sedimentary rock phosphates introduce a main source of Cd into agroecosystems (Bigalke et al., 2017; Imseng et al., 2018; Kratz et al., 2016; Kupper et al., 2014; Nziguheba and Smolders, 2008; Roberts, 2014).

Understanding the fate of fertilizer derived Cd (Cd_{dff}) in agricultural systems is crucial for assessing the risk of unintended Cd inputs into arable soils through P fertilization. Previous experiments that used mineral P fertilizers labeled with radioactive Cd showed that plants take up about 2% of the applied Cd_{dff} while 98% of it remains in the soil (Jensen and Mosbæk, 1990; Wiggenhauser et al., 2019). These results suggest that a residual Cd_{dff} pool (i.e., Cd_{dff} not taken up by the plant) may build up in the soil and may affect the soil-to-plant transfer of Cd in the crops subsequently grown on these soils. Long-term fertilization trials showed that mineral P fertilization can increase soil Cd (Cd_{soil}) concentrations, plant available Cd_{soil} pools, and Cd concentrations in

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wheat (Chaudhary et al., 2011; Grant et al., 2013; Gray et al., 2016; Hamon et al., 1998). Therefore, residual Cd_{dff} could significantly increase Cd inputs into the food chain.

Several methods can be used to assess the environmental risk of Cd_{dff}, including the risk of Cd transfer into plants and into the food chain. Temporal changes in Cd_{soil} provide information about Cd accumulation or depletion in soils (Gubler et al., 2015; Imseng et al., 2018). However, total Cd_{soil} concentrations provide limited information for environmental risk assessment because the potential Cd_{soil} mobility, i.e. the tendency of Cd to become solubilized and to enter the soil solution, varies depending on soil properties and environmental conditions (Davidson et al., 1998; Pueyo et al., 2008). Sequential extractions can partly overcome this limitation by providing information on the potential mobility of different Cd_{soil} fractions (Bacon and Davidson, 2008; Gleyzes et al., 2002; Hass and Fine, 2010). Even though the operationally defined character of the extracted fractions has been critically discussed since the introduction of sequential extractions (Nirel and Morel, 1990; Tessier and Campbell, 1991), it is widely accepted that sequential extraction procedures provide valuable information on the potentially mobilizable Cd fractions, which may become plant available under changing environmental conditions (Bacon and Davidson, 2008; McLaughlin et al., 2020; Rao et al., 2008; Rinklebe and Shaheen, 2014). However, chemical extractions (including sequential extractions) only provide limited information on the actual plant availability of Cd_{soil} (Ahnstrom and Parker, 2001; Bacon and Davidson, 2008; Kennedy et al., 1997; Nolan et al., 2003). Consequently, using target plants provides the most accurate assessment of the actual plant availability of Cd for certain species and varieties (Briat et al., 2020; Ehlers and Luthy, 2003; Semple et al., 2004). Additionally, isotopic source tracing enables the precise determination of the fate of Cd_{dff} in relevant crop production systems (Dürr-Auster et al., 2019; McBeath et al., 2013; Yan et al., 2019). Among the different isotope approaches, enriched stable isotope source tracing has the advantage that isotope ratios can be easily resolved in the sources (i.e., soil, fertilizer) and the sinks (i.e., plant), which is not always the case when using isotopes at natural abundance (Imseng et al., 2018; Wiggenhauser et al., 2019). Furthermore, recent developments in isotope mixing models enable us to determine the contributions of multiple Cd sources to Cd in a sink (Stock et al., 2018a, 2018b). Given the complementary nature of the above-mentioned methods, combining them could provide new insights into the fate of Cd_{dff} in soil-plant systems.

This study aims to obtain novel insights into the fate of Cd_{dff} in soil-fertilizer-wheat systems by investigating the partitioning of freshly applied Cd_{dff} into different system compartments (arable soil fractions and wheat plant parts). To this end, we grew wheat in pot experiments on arable soils from two long-term field trials with distinct properties and distinct past mineral P fertilizer application rates, and we applied a stable ^{111}Cd isotope labeled P fertilizer to them. We traced the freshly applied Cd_{dff} in the soils by measuring stable Cd isotope ratios in operationally defined soil fractions using a four-step sequential extraction procedure and isotopic mass balances. Furthermore, we determined the contribution of soil Cd fractions to plant Cd uptake using Bayesian isotope mixing models.

2. Materials and methods

2.1. Soils

The soils used come from two long-term field experiments conducted by Agroscope on the Swiss Plateau in Oensingen (OEN) and in Zurich (Zurich Organic Fertilization Experiment, ZOFE). Agroscope managed all the plots conventionally. The OEN soil type is a gleyic-calcaric Cambisol (IUSS Working Group WRB, 2015) that has a silty loam texture with 22.5% sand, 40.5% silt, and 37% clay in its top 20 cm (Gallet et al., 2003). The ZOFE soil type is a haplic Luvisol with a sandy loam texture with 57% sand, 27% silt and 14% clay in its top 20 cm (Leifeld and Mayer, 2015; Walther et al., 2001). Table 1 provides further information on the soils' properties.

Since the start of the field experiments, 1989 for OEN and 1949 for ZOFE, the soils received different amounts of mineral P fertilizer. The Swiss fertilization guidelines were used as a reference for the P fertilizer treatments (see SI-1). The sampled OEN soils received treatments of 33% ($OEN_{1/3}$), 100% ($OEN_{3/3}$), and 167% ($OEN_{5/3}$) of the theoretical crop P offtake through P fertilization, as defined by the Swiss fertilization guidelines (Flisch et al., 2009; Hirte et al., 2021). From the ZOFE trial, the nitrogen, phosphorus, and potassium (NPK) fertilized treatment was sampled ($ZOFE_{NPK}$). The $ZOFE_{NPK}$ fertilization (SI-1) is considered to be representative of current Swiss agriculture fertilization practices (Oberholzer et al., 2014). Soils from control plots were also sampled. In OEN, the control plots (OEN_c) did not receive any P fertilizer for 27 years. They only received N and K fertilizer at rates recommended in the Swiss fertilization guidelines (Flisch et al., 2009; Hirte et al., 2021). In the ZOFE trial, the control plots ($ZOFE_c$) were not fertilized over the entire 67 year period (Leifeld and Mayer, 2015). Details on the long-term fertilization trials and the sampling method are provided in SI-1.

2.2. Fertilizer labeling

A commercial triple superphosphate fertilizer containing 201 g P kg^{-1} was isotopically labeled using an enriched ^{111}Cd spike, following the protocol described in Wiggenhauser et al. (2019). SI-2 describes the labeling procedure in more detail. ^{111}Cd was chosen as tracer isotope due to the absence of isobaric interferences (Rehkämper et al., 2012) and because it is comparably cheap when compared with less abundant Cd isotopes (Larner and Rehkämper, 2012). Although the natural abundance of ^{111}Cd is relatively high at 12.8% (Berglund and Wieser, 2011), it nevertheless enables a sufficient resolution of the isotope ratios in the soil-fertilizer-wheat systems because the fertilizer is directly labeled with a highly enriched ^{111}Cd spike (Dürr-Auster et al., 2019). ^{110}Cd was chosen due to the almost complete elimination of palladium (Pd) during ion-exchange chromatography (see section 2.6) which strongly reduced isobaric interference by ^{110}Pd. ^{110}Cd was also chosen due to high tin (Sn) background concentrations that can make individual Sn isotope interference correction on ^{112}Cd, ^{114}Cd and ^{116}Cd inappropriate.

The labeled fertilizer had a Cd concentration of 50.9 ± 1.4 µg Cd g^{-1}, which corresponds to the upper end of Cd concentrations found among commercial P fertilizers in the European Union (Kratz et al., 2016; Verbeeck et al., 2020). The $^{111}Cd/^{110}Cd$ isotope ratio in the pseudo-totally digested labeled fertilizer of 59.174 was significantly different from the $^{111}Cd/^{110}Cd$ isotope ratio of 1.025 at natural abundance (Berglund and Wieser, 2011). All fractions of the fertilizer were homogeneously labeled (SI-3). The fertilizer's mineralogy changed during the labeling procedure (SI-3) and we therefore consider the labeled fertilizer to be a model fertilizer and not an equivalent to the unlabeled mineral P fertilizer. Nonetheless, the water solubility of the Cd in the labeled fertilizer was high (45% versus 55% in the original triple superphosphate fertilizer), and about 93% of the Cd in the fertilizer was potentially mobile (see SI-3). The realistic Cd concentration and its high solubility make the labeled model fertilizer of practical relevance (McLaughlin et al., 2020). SI-3 provides further information on the labeled fertilizer.

2.3. Plant growth experiment

Four replicate pots with 1 kg soil (dry weight) per past mineral P fertilizer treatment were prepared, resulting in a total of 24 pots. We applied 502 ± 1 mg of finely ground labeled fertilizer to the soil equally and mixed it thoroughly, resulting in concentrations of 99 mg P and 25.5 ± 0.1 µg Cd kg^{-1} soil. To ensure regular plant growth in all soils, nutrient solutions containing 674 mg $Ca(NO_3)_2$, 57 mg NH_4NO_3, 304 mg

Table 1
Selected properties of the soils used in this study.

Treatment		Cd_{soil}[a]	Cd_{dff} of total Cd[b]	pH	ECEC[c]	BS[d]	SOC[e]	Fe_{tot}[f]
		ng g^{-1}	%	$CaCl_2$	$mmol_c$ kg^{-1}	%	%	%
OEN	c	333 ± 4[c]	7.1 ± 0.1[c]	6.6	232	99.8	2.3	2.7
	1/3	353 ± 9[d]	6.7 ± 0.1[b]	6.8	317	100	2.3	2.7
	3/3	362 ± 7[d]	6.6 ± 0.1[b]	6.6	261	100	2.3	2.7
	5/3	370 ± 1[e]	6.4 ± 0.0[a]	6.7	319	100	2.3	2.7
ZOFE	c	224 ± 3[b]	10.2 ± 0.1[d]	4.5	52	93.1	0.7	1.2
	NPK	191 ± 6[a]	11.7 ± 0.3[e]	4.7	63	97.1	0.8	1.3

[a] Median soil Cd concentration of bulk soil before the addition of the labeled fertilizer. Median absolute deviation of n = 4 samples. The letters indicate the significant differences between the medians.
[b] Cd_{dff} concentration as percentage of the pseudo-total Cd concentration in a soil sample (i.e., Cd_{soil} + Cd_{dff}). Each pot of 1 kg of soil received 25.5 ± 0.1 μg Cd.
[c] Effective cation exchange capacity (ECEC) determined in 1 mol L^{-1} NH_4NO_3 using a 1:20 (m:v) ratio after 1 h of equilibration.
[d] Base saturation (BS) was calculated as a percentage share of Ca, Mg, and K concentrations of the summed concentration of Ca, Mg, K, Mn, and Al in filtrates for the ECEC. Na was not included in the ECEC nor BS calculations due to high Na background concentrations in blank samples.
[e] Soil organic carbon (SOC) concentrations were determined by combusting soil samples that were previously heated to 105 °C and 550 °C in an elemental analyzer (vario EL cube, Elementar Analysensysteme GmbH, Langenselbold, DE).
[f] Total iron (Fe) concentrations were determined using X-ray fluorescence spectroscopy (Niton XL2 XRF Analyzer, Thermo Scientific, Waltham, MA, US).

$MgSO_4$, and 120 mg K_2SO_4 were applied to each pot. N was applied at high rates because of reported N-limitation in the plant growth of the $ZOFE_c$ treatment (Grüter et al., 2019; Oberholzer et al., 2014). Two pre-germinated wheat seedlings (*Triticum aestivum* L. cv. Fiorina) were planted per pot and were then thinned to one seedling after one week. All pots were randomly placed in a growth chamber and were re-randomized every other week. The plants grew in a simulated environment that had 14 h of daylight using 25 kilolux luminous flux, a relative humidity of 60%, and a temperature of 24 °C. All of the pots were watered with deionized water every other day to 60% of their water holding capacity.

2.4. Sample preparation

Soils and plant parts were sampled after 97 days at full plant maturity. Plants were cut approximately 15 mm above the soil surface with ceramic scissors, rinsed with deionized water and sorted into straw and grains. Straw included all of the above-ground plant parts except the grains. Leaf parts with soil contamination were removed. The removed leaf parts only constituted a very small part of the sample and did not significantly influence the Cd mass balances. Roots were carefully separated from the soil by sieving (<5 mm) and then subsequently rinsed with deionized water and washed for 15 min in 6 mM $NaNO_3$ at 4 °C to disperse adherent soil particles and to desorb Cd from the root apoplast (Böhm, 1979; Wiggenhauser et al., 2016). All soil samples and plant parts were transferred to paper bags and dried for 5 day at 50 °C. All plant parts were ground into a fine powder using agate or tungsten carbide ball mills. Soil samples were separated from the remaining fine roots and sieved to fine soil (<2 mm).

To analyze the Cd in plant samples, 200 mg aliquots of ground roots and 400 mg aliquots of ground straw and grains were digested using 4 mL 7.5 mol L^{-1} HNO_3 in a single reaction chamber microwave (UltraCLAVE, Milestone, Shelton, CT, US) for 15 min at 120 bar and 200 °C and for 12 min at 250 °C. After digestion, the samples were stored at 4 °C to await further processing. SI-7 provides data on the quality control of the digestion procedure.

2.5. Cd in soils and the sequential extraction of Cd

Cd was extracted from the soil samples by applying the revised four-step sequential extraction procedure developed by Rauret et al. (1999) for the Commission of the European Communities' Community Bureau of Reference (BCR), subsequently referred to as the revised BCR sequential extraction scheme (Table 2). In the revised BCR sequential extraction scheme, Cd is successively extracted under conditions that mimic environmental changes such as soil acidification (fraction F1), changes in redox conditions (reduction due to e.g., waterlogging (F2) and oxidation due to e.g., ploughing (F3)) or long-term weathering (F4) (Bacon and Davidson, 2008; Davidson, 2013; Filgueiras et al., 2002; Gleyzes et al., 2002; Hass and Fine, 2010). Approximately 500 mg of dry fine soil were weighed into 50 mL polypropylene centrifuge tubes. The extractants described in Table 2 were then added. Soil-extractant suspensions were shaken for 16 h at room temperature on an end-over-end shaker at a speed of 20 rpm. Subsequently, the tubes were centrifuged for 20 min at 3000 g. The supernatant was decanted into separate polypropylene tubes. The soil that remained after the F3 extraction was pseudo-totally digested in *aqua regia* to extract F4 (Table 2). SI-4 and SI-7 provide detailed information on the sequential extraction procedure and quality control.

Table 2
Revised BCR sequential extraction procedure (Rauret et al., 1999).

Fraction		Extractant
F1	Acetic acid soluble	20 mL 0.11 mol L^{-1} acetic acid (CH_3COOH); 16 h shaking
F2	Reducible	20 mL 0.5 mol L^{-1} hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) at pH 1.5; 16 h shaking
F3	Oxidizable	10 mL 8.8 mol L^{-1} hydrogen peroxide (H_2O_2) at 85 °C followed by 25 mL 1.0 mol L^{-1} ammonium acetate (CH_3COONH_4) at pH 2; 16 h shaking
F4/pseudo-total	Inert	10 mL *aqua regia* (10.4 mol L^{-1} HCl + 15.5 mol L^{-1} HNO_3, v:v = 3:1)

Cd partitioned into F1 is considered to be weakly adsorbed or co-precipitated with carbonates and readily mobilized by ion-exchange processes or by the lowering of the soil pH (Filgueiras et al., 2002). Cd partitioned into F2 is thought to be mostly bound to reducible soil phases such as Fe and Mn hydroxides (Chao and Zhou, 1983; Davidson, 2013; Mossop and Davidson, 2003). Cd sorbed to Fe and Mn hydroxides can be incorporated into metal oxide structures, and substantial shares of Cd are not readily desorbed (Backes et al., 1995; Fischer et al., 2007). Cd partitioned into F3 is considered to be associated with organic matter and sulfides (Gleyzes et al., 2002; Mossop and Davidson, 2003; Ure and Davidson, 2007). However, Cd associated with hydroxides or organic matter is already partly extracted in the previous steps and F2 and F3 therefore do not selectively represent the oxide and organically bound Cd fractions (Bacon and Davidson, 2008; Meers et al., 2007). Cd partitioned into F4 is considered to be inert and bound in mineral's crystalline lattices (Gleyzes et al., 2002). It is generally considered that the potential mobility of sequentially extracted Cd decreases from F1 to F4 (Bacon and Davidson, 2008; Rinklebe and Shaheen, 2014).

2.6. Determining Cd concentrations and Cd isotope ratios in labeled samples

Prior to the mass spectrometric isotope analysis, the plant and soil samples were purified by anion exchange resin chromatography (Cloquet et al., 2005). In short, the digested samples were evaporated, re-dissolved in 1.2 mol L^{-1} HCl, and loaded on 2 mL resin (Biorad® AG MP-1). The matrix elements were subsequently eluted from the sample using 1.2, 0.3 and 0.012 mol L^{-1} HCl. Lastly, Cd was eluted using 0.0012 mol L^{-1} HCl.

Cd concentrations and isotope ratios were analyzed using a single collector quadrupole inductively coupled plasma mass spectrometer (Q-ICP-MS 7700x, Agilent Technologies, Santa Clara, CA, US). Quality control and quality improvement was done by periodical measurements of the standard solutions and the proportional correction of the signal drifts. SI-5 provides further information on determining Cd concentrations in labeled samples.

2.7. Calculation of Cd_{dff} recoveries in plant parts and soil fractions

The fractions of Cd in the soil extracts (F1–F4) and in the plants derived from the labeled fertilizer were calculated using an adapted isotope mass balance equation developed by McBeath et al. (2013) (Eq. (1)):

$$f_{Cd_{dff}} = \frac{NA_{110} \times IR_{sample} - NA_{111}}{(SA_{111} - NA_{111}) - IR_{sample} \times (SA_{110} - NA_{110})} \quad \text{(Eq. 1)}$$

where $f_{Cd_{dff}}$ denotes the fraction of labeled fertilizer derived Cd, ranging from 0 to 1. NA denotes the natural abundances of ^{110}Cd (0.125) and ^{111}Cd (0.128), SA is the specific abundances of ^{110}Cd (0.015) and ^{111}Cd (0.882) in the labeled fertilizer, and IR_{sample} is the $^{111}Cd/^{110}Cd$ isotope ratio in a sample. Published values were used for the natural abundances of ^{110}Cd and ^{111}Cd (Berglund and Wieser, 2011). The $f_{Cd_{dff}}$ in the sample allows the recovery percentage of the freshly applied Cd_{dff} in the respective sample ($\%Cd_{dff\_recovery}$) to be calculated (Eq. (2)):

$$\%Cd_{dff_{recovery}} = \frac{f_{Cd_{dff}} \times Cd_{sample}}{Cd_{dff_{applied}}} \times 100 \quad \text{(Eq. 2)}$$

with Cd_{sample} designating the mass of Cd in the soil or plant sample (in μg Cd kg^{-1}) and $Cd_{dff\_applied}$ denoting the total mass of Cd_{dff} applied through the labeled fertilizer (25.5 ± 0.1 μg Cd_{dff} kg^{-1} soil). All % $Cd_{dff\_recovery}$ values reported in this study refer to $Cd_{dff\_applied}$ with the labeled fertilizer.

2.8. Isotope mixing model: sources of Cd in wheat

The contribution of the soil fractions to Cd in the wheat shoots was assessed by modelling possible mixtures of the $^{111}Cd/^{110}Cd$ isotope ratios in the four soil fractions that result in the $^{111}Cd/^{110}Cd$ isotope ratios in wheat shoots. The modelling was done using the Bayesian stable isotope mixing model MixSIAR (version 3.1.10) in the *R* software (Stock et al., 2018a; Stock and Semmens, 2016). SI-6 provides further information on the Bayesian mixing models.

Stable isotope mixing models have been demonstrated to serve as valuable tools for assessing metal(loid) sources in arable soils at different spatial scales, from individual fields to catchment areas (Kitch et al., 2019; Kong et al., 2018; Salmanzadeh et al., 2017; Wang et al., 2021; Zhang et al., 2020). This mixing model approach has been mostly used to conduct source tracing using stable metal isotopes at natural abundance. In this study, we apply the approach for an enriched stable isotope source tracing experiment. Enriched stable isotopes are particularly interesting in pot experiments or at (sub-)plot levels. In large scale studies such as at catchment or ecosystem levels, large quantities of enriched stable isotopes would need to be added to successfully trace the added Cd_{dff} due to the greater dilution of the enriched isotope signal over larger distances, which would cause high costs and analytical efforts.

2.9. Statistical analysis

The data was tested for normality using the Shapiro-Wilk test and for homogeneity of variances using Levene's test. Given that some data series showed non-normal distribution, all data was analyzed using the non-parametric Kruskal-Wallis test. Post-hoc multiple comparison procedures were conducted using Conover's test, with a p-value adjustment based on Benjamini and Hochberg (1995). For all tests, $\alpha = 0.05$ was set as the critical value for the null hypothesis of no significant differences. The central tendency is presented as the median, and the dispersion is presented as the median absolute deviation with a scaling factor of 1. The median absolute deviation is a robust measure of dispersion due to its insensitivity to outliers and non-normal data distribution (Leys et al., 2013; Pham-Gia and Hung, 2001). All statistical analyses were conducted in *R* (version 3.4.2 (R Core Team, 2018)).

3. Results

3.1. Soil Cd concentrations and the partitioning of Cd in soil fractions

Cd_{soil} concentrations were significantly different between the two soils (OEN and ZOFE) as well as between the different past mineral P treatments (Table 1). There was an increase in Cd_{soil} concentrations in the OEN soil when the past mineral P fertilizer application rates were increased from OEN_c to $OEN_{5/3}$ (Table 1). In the ZOFE soil, there were lower Cd_{soil} concentrations in the fertilized $ZOFE_{NPK}$ when compared with the unfertilized $ZOFE_c$ treatment (Table 1).

Cd_{soil} concentrations partitioned into F1 differed depending on the past mineral P treatments in OEN and in ZOFE (Fig. 1). In the OEN treatments, the median Cd_{soil} concentration in F1 increased from 79.5 ± 0.8 ng Cd g^{-1} in OEN_c to 86.9 ± 1.4 ng Cd g^{-1} in $OEN_{5/3}$ (Fig. 1). In ZOFE, the largest differences between the two past treatments were found in F1 with 73.1 ± 1.5 ng Cd g^{-1} in the ZOFENPK and 94.6 ± 0.2 ng Cd g^{-1} in the ZOFEc treatment (Fig. 1). The largest share of Cd_{soil} in the OEN soil was partitioned into F2. No differences were found in the partitioning of Cd_{soil} into F2 between the different past mineral P treatments within OEN and ZOFE (Fig. 1). Only slight differences were found in F3 and F4 in the OEN treatments but not in ZOFE (Fig. 1).

The percentage contributions of the four fractions to the pseudo-total Cd_{soil} concentration showed that Cd_{soil} was equally partitioned into F1 and F2 in the ZOFE soil and that F2 was the predominant Cd_{soil} fraction in the OEN soil (Table 3). Cd_{soil} partitioned into F3 and F4 accounted for less than 10% of Cd_{soil} in both OEN and ZOFE. Table 3 summarizes the results of the relative partitioning of Cd_{soil} in OEN and ZOFE.

3.2. Plant Cd uptake and concentrations

In the OEN treatments, total Cd concentrations in all plant parts increased when the past mineral P fertilizer application rates increased from $OEN_{1/3}$ to $OEN_{5/3}$ (SI table 4). Cd concentrations in the shoots increased from 47.3 ± 2.8 ng g^{-1} dry matter in $OEN_{1/3}$ to 57.9 ± 3.3 ng g^{-1} in $OEN_{5/3}$. In grains, Cd concentrations increased from 30.6 ± 1.3 ng g^{-1} dry matter in $OEN_{1/3}$ to 44.6 ± 1.7 ng g^{-1} in $OEN_{5/3}$ (SI table 4). Cd concentrations in the shoots and in the whole plant on the P unfertilized OEN_c did not differ from $OEN_{5/3}$ despite lower Cd_{soil} concentrations in OEN_c (SI table 4). In the ZOFE treatments, Cd concentrations were higher in the shoots and in the whole plant on the unfertilized $ZOFE_c$ compared with $ZOFE_{NPK}$ (SI table 4). Cd concentrations in the shoots were 137.7 ± 11.7 ng g^{-1} on $ZOFE_c$ and 78.9 ± 5.4 ng g^{-1} on $ZOFE_{NPK}$ (SI table 4).

Plant uptake of Cd was lower in OEN than in ZOFE soils. In OEN, Cd uptake by the whole plant increased from 1.61 ± 0.07 μg Cd in $OEN_{1/3}$ to

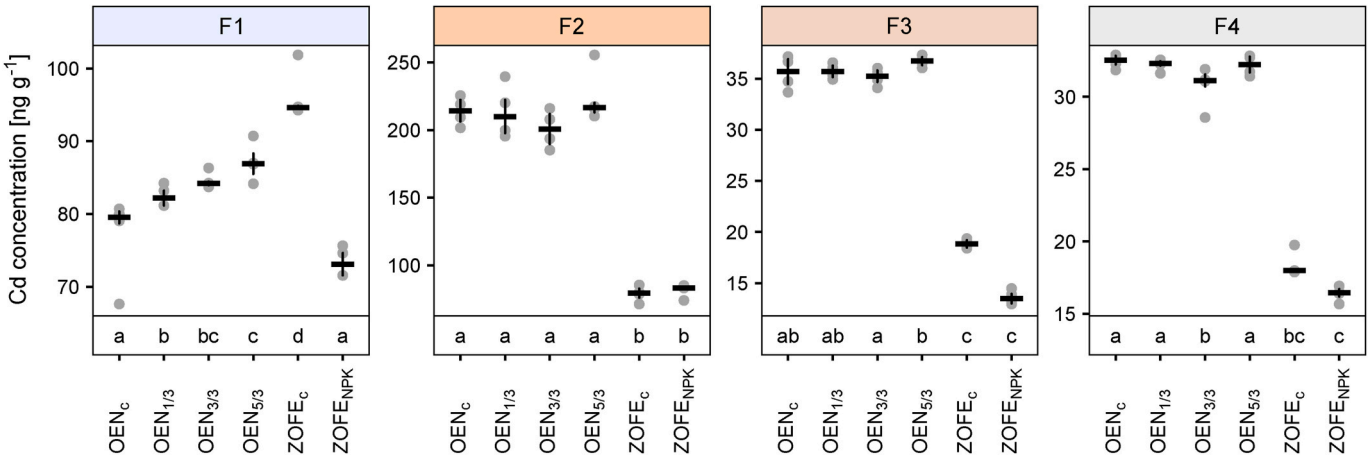

Fig. 1. Median partitioning of Cd_{soil} concentrations [ng Cd g^{-1} soil] into four soil fractions (F1–F4). F1 denotes acetic acid soluble Cd, F2 reducible Cd, F3 oxidizable Cd and F4 inert Cd. OEN (Oensingen) and ZOFE (Zurich) indicate the origin of the soil samples. Past mineral P fertilizer treatments are indicated by the subscripts. For OEN, "1/3" (33%), "3/3" (100%), and "5/3" (167%) indicate the mineral P fertilizer rates relative to the theoretical crop P offtake. For ZOFE, "NPK" indicates a standard NPK fertilization. Control plots are indicated by the letter "c". SI-1 provides more details on the past fertilizer treatments. There are n = 4 samples per treatment. Horizontal lines indicate the median Cd concentration. Whiskers indicate the median absolute deviation. Gray dots represent the Cd concentrations in the individual soil samples. The different letters under the plots indicate the significant differences ($p < 0.05$) between the medians determined using the Kruskal–Wallis test.

Table 3
Median partitioning of Cd_{soil} and Cd_{dff} in the soil fractions and plant parts of wheat.

System compartment		Cd_{soil}		Cd_{dff}	
		OEN	ZOFE	OEN	ZOFE
		%	%	%	%
Wheat	Whole plant	–	–	1.0 ± 0.1^{a}	2.3 ± 0.1^{b}
	Shoots	–	–	0.5 ± 0.0^{a}	1.2 ± 0.1^{b}
	Grains	–	–	0.2 ± 0.0^{a}	0.3 ± 0.0^{b}
	Straw	–	–	0.3 ± 0.0^{a}	0.9 ± 0.1^{b}
	Roots	–	–	0.4 ± 0.0^{a}	1.0 ± 0.0^{b}
Soil	F1	22.9 ± 0.6^{a}	42.8 ± 2.8^{b}	41.1 ± 5.1^{a}	60.9 ± 2.6^{b}
	F2	58.4 ± 1.0^{a}	40.3 ± 3.2^{b}	64.5 ± 8.9^{a}	32.9 ± 3.7^{b}
	F3	9.9 ± 0.3^{a}	8.1 ± 0.7^{a}	3.9 ± 0.4^{a}	2.1 ± 0.1^{b}
	F4	8.8 ± 0.2^{a}	8.8 ± 0.1^{a}	0.6 ± 0.1^{a}	0.6 ± 0.1^{a}

Median values and median absolute deviations of the relative partitioning (%) of Cd_{soil} and Cd_{dff}. Cd_{soil} denotes Cd present in the soil before the addition of Cd with the labeled fertilizer (Cd_{dff}). There are n = 16 samples for OEN and n = 8 samples for ZOFE. F1 denotes acetic acid soluble Cd, F2 reducible Cd, F3 oxidizable Cd, and F4 inert Cd. OEN (Oensingen) and ZOFE (Zurich) indicate the origin of the samples. The different letters indicate significant differences ($p < 0.05$) between the medians of OEN and ZOFE determined using the Kruskal–Wallis test.

2.13 ± 0.04 µg Cd in $OEN_{5/3}$ (SI table 4). The Cd uptake by the whole plant in OEN_c (1.84 ± 0.07 µg Cd) was also lower than in $OEN_{5/3}$. Cd uptake by shoots in OEN, however, only increased in $OEN_{5/3}$. The dry matter weight of the whole plants did not influence the soil to plant transfer of Cd as there was only a difference in dry matter weights between OEN_c and $OEN_{5/3}$ (SI table 4). The dry matter weight of the shoots differed between the past mineral P treatments and might have influenced the soil to plant transfer of Cd (SI table 4).

In ZOFE, dry matter weight was higher in $ZOFE_{NPK}$ than in $ZOFE_c$ while the Cd uptake of the whole plant and the shoots was higher in $ZOFE_c$ (whole plant: 3.92 ± 0.27 µg Cd; shoots: 2.24 ± 0.23 µg Cd) than in $ZOFE_{NPK}$ (whole plant: 3.07 ± 0.20 µg Cd; shoots: 1.62 ± 0.14 µg Cd) (SI table 4). The higher Cd uptake in $ZOFE_c$ was related to the higher Cd concentration in wheat, which outbalanced the lower dry matter weight of this treatment.

Cd concentrations in the different plants parts successively decreased from root > shoot > grains (SI table 4), as had been previously observed for wheat (Grant et al., 1998; Wiggenhauser et al., 2016). SI table 4 provides additional information on Cd uptake and concentrations in the different plant parts of wheat (roots, straw, grains).

3.3. Partitioning of fresh fertilizer derived Cd in soils

For some OEN samples, there was considerable variability in the $^{111}Cd/^{110}Cd$ ratios as input values for the calculation of the $\%Cd_{dff\_recovery}$. These input values led to overall $\%Cd_{dff\_recovery}$ values of over 100%, ranging from 107.0 ± 6.3% in $OEN_{5/3}$ to a maximum of 130.5 ± 30.4% in $OEN_{1/3}$ (n = 4 each). For all OEN samples, the overall $\%Cd_{dff\_recovery}$ was 109.5 ± 14.4% (n = 16). This variability is within the range of commonly reported recoveries in sequential extractions (Ho and Evans, 2000; Mester et al., 1998; Rinklebe and Shaheen, 2014) but is high for a tracing experiment. Based on the finding that the $^{111}Cd/^{110}Cd$ ratio was consistently elevated in all of the fractions of soil samples that had considerably high $\%Cd_{dff\_recovery}$ values (SI Table 3), we assume that small residues of the labeled fertilizer remained undissolved in the neutral OEN soil and that complete dissolution occurred in the strongly acidic ZOFE soil. The dissolution of fertilizer residues that had a high $^{111}Cd/^{110}Cd$ ratio in the sequential extraction therefore led to a disproportional increase of the $^{111}Cd/^{110}Cd$ ratio in some OEN extracts. The sensitivity of the mass balances means that even small deviations in the ^{111}Cd labeling of the soil matrix can distort the calculated $\%Cd_{dff\_recovery}$ values (Gäbler et al., 2007). Nonetheless, the $\%Cd_{dff\_recovery}$ in the different soil fractions showed distinct patterns that allow for conclusions to be drawn about the partitioning of Cd_{dff} in the different soils.

Cd_{dff} partitioning patterns in the soils differed significantly between OEN and ZOFE (Table 3). Less Cd_{dff} was partitioned into the acetic acid soluble F1 in the OEN soil compared with the ZOFE soil (19.8% median difference) (Table 3). The partitioning of Cd_{dff} into the reducible F2 followed a pattern that was opposite to that of the F1. The $\%Cd_{dff\_recovery}$ in F2 was higher in OEN compared with ZOFE (31.6% median difference) (Table 3). Only a minor share of Cd_{dff} was partitioned into the oxidizable F3 and the inert F4 in both soils. The $\%Cd_{dff\_recovery}$ in F3 was higher in OEN than in ZOFE (1.8% median difference) (Table 3). In both soils, the $\%Cd_{dff\_recovery}$ in F4 was less than 0.7%.

3.4. Source tracing of Cd in wheat

Less than 2.3% of the freshly applied Cd_{dff} was recovered in the wheat plants (Table 3). The $\%Cd_{dff\ recovery}$ was lower in the whole plant as well as in the shoots on the OEN (1.0% and 0.5%, respectively) compared with the ZOFE soil (2.3% and 1.2%, respectively) (Table 3). In OEN, the $\%Cd_{dff\ recovery}$ increased with the increased past mineral P application rates in the whole plant, roots and grains (Fig. 2 and SI table 4) but not in the overall shoots (Fig. 2). There were no differences in the $\%Cd_{dff\ recovery}$ for any plant part between the ZOFE treatments (SI table 4 and Fig. 2).

By using the MixSIAR Bayesian stable isotope mixing models, $^{111}Cd/^{110}Cd$ ratios in the shoots were used to determine the soil fractions' contributions to the Cd in the wheat shoots (Stock et al., 2018a, 2018b). Due to the variability observed in the $^{111}Cd/^{110}Cd$ ratios of the OEN samples, the mixing models were run per soil by aggregating all past P fertilizer treatments for each soil. Neither location showed a difference between the $^{111}Cd/^{110}Cd$ ratios in shoots and in F1 (Fig. 3). All other fractions showed different $^{111}Cd/^{110}Cd$ ratios compared to the ratios in the shoots (Fig. 3).

The variability between the $^{111}Cd/^{110}Cd$ ratios led to a considerable variability in the modeled Cd contributions from the different soil fractions to the Cd in the wheat shoots. Nonetheless, it was possible to identify clear tendencies. The mixing models indicated that in OEN, 84.3 ± 4.7% of Cd in shoots originated from F1 and that 6.9 ± 4.3% originated from F2 (Fig. 3). In ZOFE, the model yielded similar results: 81.7 ± 6.5% of Cd originated from F1 and 7.3 ± 4.8% originated from F2 (Fig. 3). All models showed that less than 5% of the Cd in shoots originated from either F3 or F4.

4. Discussion

4.1. Crop management controls the Cd accumulation rate in the soils

Recently obtained Cd mass balances in Swiss arable systems revealed that crop offtake and P fertilization in current agricultural practices are the major factors that determine Cd_{soil} accumulation (Imseng et al., 2018). In this study, over 97.7% of freshly applied Cd_{dff} remained in the soil. This underlines the significance of Cd concentrations in fertilizers as Cd inputs into arable soils. Frequent applications of mineral P fertilizers that contain high Cd concentrations may therefore lead to an accumulation of Cd in soils in the long term (Six and Smolders, 2014; Smolders, 2017). However, Cd_{soil} concentration in the mineral P fertilized $ZOFE_{NPK}$ treatment was 14.7% lower than in the unfertilized $ZOFE_c$ (Table 1). Recent Cd balances in ZOFE by Grüter et al. (2019) revealed that dry weight biomass production was about four times higher on $ZOFE_{NPK}$ compared to $ZOFE_c$ (shoot biomass of 6.4 t ha^{-1} on $ZOFE_{NPK}$ and 1.7 t ha^{-1} on $ZOFE_c$) while Cd offtake with the harvest was about three times higher on $ZOFE_{NPK}$ than on $ZOFE_c$ (1.49 g Cd ha^{-1} y^{-1} on $ZOFE_{NPK}$ and 0.49 g Cd ha^{-1} y^{-1} on $ZOFE_c$). As a result, large Cd outputs through Cd crop offtake may have outweighed Cd inputs through mineral P fertilizer in the $ZOFE_{NPK}$ treatment.

Unlike in ZOFE, Cd_{soil} concentrations in OEN increased by 5.9% ($OEN_{1/3}$) to 11.1% ($OEN_{5/3}$) with the increase of past mineral P

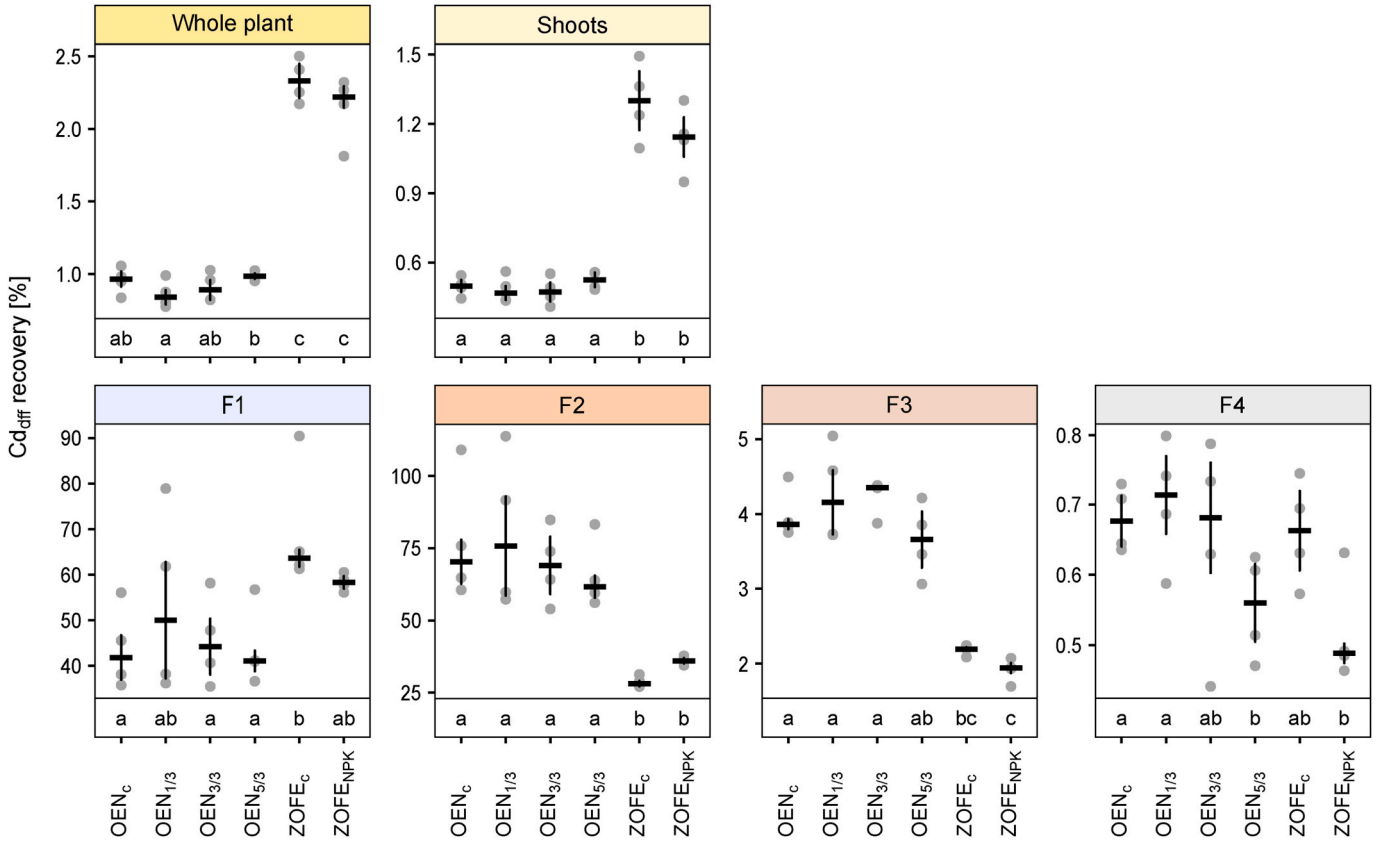

Fig. 2. Median percentage recoveries of freshly added Cd_{dff} in the whole wheat plant, the wheat shoots, and the soil fractions (F1–F4) by different past mineral P fertilizer applications. F1 denotes acetic acid soluble Cd_{dff}, F2 reducible Cd_{dff}, F3 oxidizable Cd_{dff} and F4 inert Cd_{dff}. OEN (Oensingen) and ZOFE (Zurich) indicate the origin of the soil samples. Past mineral P fertilizer treatments are indicated by the subscripts. For OEN, "1/3" (33%), "3/3" (100%), and "5/3" (167%) indicate the mineral P fertilizer rates relative to the theoretical crop P offtake. For ZOFE, "NPK" indicates a standard NPK fertilization. Control plots are indicated by the letter "c". SI-1 provides more details on the past fertilizer treatments. There are n = 4 samples per treatment. Horizontal lines indicate the median Cd_{dff} recovery. Whiskers indicate the median absolute deviation. Gray dots represent the percentage Cd_{dff} recovery in individual samples. The different letters under the plots indicate the significant differences ($p < 0.05$) between the medians determined using the Kruskal–Wallis test.

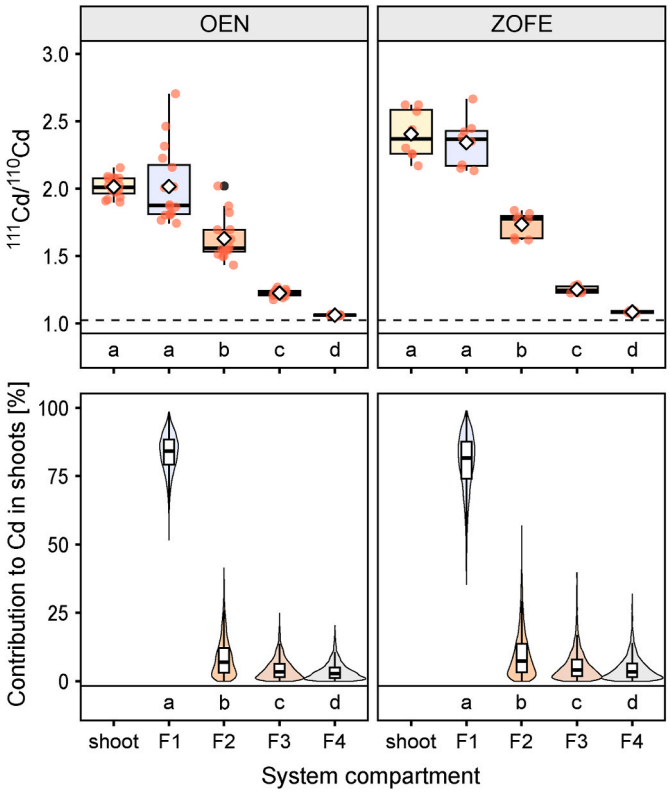

Fig. 3. $^{111}Cd/^{110}Cd$ isotope ratios in shoots and soil fractions (upper graphs) and relative contribution of Cd derived from the different soil fractions (F1–F4) to Cd in wheat shoots (lower graphs). F1 denotes acetic acid soluble Cd, F2 reducible Cd, F3 oxidizable Cd, and F4 inert Cd. OEN (Oensingen) and ZOFE (Zurich) indicate the origin of the soil samples. There are n = 16 samples for OEN and n = 8 samples for ZOFE. In the upper graphs, the horizontal dashed line indicates the $^{111}Cd/^{110}Cd$ isotope ratio at natural abundance of 1.025 (Berglund and Wieser, 2011), the rhombi indicate the mean, and the jittered red dots represent the $^{111}Cd/^{110}Cd$ isotope ratios in individual samples. In the lower graphs, the violin plots show the frequency of the modeled contributions of a soil fraction to Cd in shoots. For all boxplots, whiskers indicate the 1.5- times interquartile range, horizontal solid lines denote the median, and black dots represent outliers. The different letters under the plots indicate the significant differences ($p < 0.05$) between the medians determined using the Kruskal–Wallis test. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

applications when compared with the OEN_c treatment (Table 1). Additionally, Cd_{soil} concentrations in F1 rose with increasing past mineral P applications, whereas no increase was observed in the other fractions (Fig. 1), in accordance with findings of Gray et al. (1999). These results strongly suggest that repeated past mineral P inputs mainly increased the most easily mobilizable Cd_{soil} fraction in OEN. However, Cd concentrations in the shoots on $OEN_{3/3}$ and $OEN_{5/3}$ were not different from OEN_c (SI table 4). Furthermore, there was only a significant increase in Cd uptake if mineral P fertilizer was formerly applied at higher rates than crop P offtake (i.e., $OEN_{5/3}$) (SI table 4). Our observations are in line with recently obtained Cd mass balances in typical Swiss arable systems that revealed that, under current agricultural practices, Cd_{soil} mass balances can be slightly positive or negative depending on the crop (Imseng et al., 2018). Overall, our results demonstrate that past mineral P applications did not increase the risk of Cd inputs into the food chain when the soils were fertilized to balance crop P offtake (i.e., $OEN_{3/3}$), whereas surplus mineral P applications (i.e., $OEN_{5/3}$) increased Cd_{soil} and plant Cd concentrations.

4.2. Low recovery of fertilizer derived Cd in wheat

We traced the ^{111}Cd isotope label in the fertilizer in soil-wheat systems using isotope mass balances. In the case of nutrients, this method is used to quantify the efficiency of a fertilizer by precisely assessing the recovery of a fertilizer applied nutrient in the plant (Dürr-Auster et al., 2019; McBeath et al., 2013). For a contaminant such as Cd, the recovery provides information on its fate in soil-plant systems and its transfer into the food chain. The low $\%Cd_{dff\_recovery}$ values of 0.5–1.2% in shoots (Fig. 2) is in the same range as the $\%Cd_{dff\_recovery}$ values of 0.5–2.2% for wheat (Wiggenhauser et al., 2019) and of 0.9–1.2% for lettuce (Jensen and Mosbæk, 1990). The significantly higher $\%Cd_{dff\_recovery}$ in the shoots in ZOFE than in the shoots on OEN soils can be explained by the lower soil pH, soil organic carbon concentrations and cation exchange capacity in the ZOFE soil (Table 1). Among these soil properties, pH is generally regarded as a major determining factor for plant Cd uptake (Degryse et al., 2009; Smolders and Mertens, 2013) because Cd_{soil} is increasingly solubilized and becomes more plant available with lower soil pH (Sauvé et al., 2000). Similarly, mineral P fertilizer dissolution is mainly a function of soil pH and Ca^{2+} activity, which results in a more efficient dissolution at lower soil pH (Chien et al., 2011; Mengel et al., 2001; Prochnow et al., 2008). These reasons explain why the labeled fertilizer was more efficiently dissolved in the strongly acidic ZOFE soils while at the same time fewer cation binding sites on soil phases were available (He and Singh, 1993). Consequently, a larger share of Cd_{dff} was plant available in the strongly acidic ZOFE soils than in the neutral OEN soils.

4.3. Soil pH and reducible phases determine potential mobility of fertilizer derived Cd in soil

To obtain more detailed information on the fate of the freshly added Cd_{dff} in the soil, we measured $^{111}Cd/^{110}Cd$ ratios in different operationally defined soil fractions and in wheat shoots. We complemented these analyses using Bayesian isotope mixing models to identify the contribution of each soil fraction to Cd in the shoots. In all soil samples, over 95% of the total applied Cd_{dff} was partitioned into the acetic acid soluble F1 and the reducible F2 (Fig. 2 and Table 3). However, the partitioning into these two fractions differed significantly between the two soils depending on their properties. The distinct $\%Cd_{dff\_recovery}$ patterns in ZOFE (F1>F2≫F3>F4) and in OEN (F2>F1≫F3>F4) indicate a higher potential Cd_{dff} mobility in the ZOFE than in the OEN soil.

Cd_{dff} partitioned into F1 represents the most easily mobilizable fraction (Bacon and Davidson, 2008). The high $\%Cd_{dff\_recovery}$ values in F1 in both soils are consistent with the common finding that Cd is among the most mobile heavy metals in soils (Ho and Evans, 2000; Li et al., 2010; Smolders and Mertens, 2013) and also reflects the high solubility of the mineral P fertilizer (SI-3). Soil pH is the governing factor in the partitioning of Cd_{dff} into F1, as shown by the significantly higher $\%Cd_{dff\_recovery}$ in F1 in the highly acidic ZOFE soil (Table 3) (McGrath, 1996; Renella et al., 2004; Sauvé et al., 2000; Sterckeman et al., 2009). Additionally, the isotopic mixing models revealed that F1 was the predominant source of the Cd recovered in the shoots on both soils. More than 80% of the Cd taken up by the plant originated from F1 (Fig. 3). Our results confirm that F1 of the revised BCR sequential extraction scheme can be a good indicator of a potentially plant available Cd pool in soils (Meers et al., 2007; Sahuquillo et al., 2003). The correspondingly higher $\%Cd_{dff\_recovery}$ in F1 and in the shoots in ZOFE compared with those in OEN exemplifies this finding (Fig. 2). Because the effects of Cd ageing in the soil are negligible at a pH below 6.5 (Smolders et al., 1999; Smolders and Mertens, 2013; Tye et al., 2003), the high recovery of Cd_{dff} in F1 suggests that a large share of freshly applied Cd_{dff} remains potentially plant available for the following crop cycle.

The dominant role of the reducible F2 in the $\%Cd_{dff\_recovery}$ in OEN compared to in ZOFE (Fig. 2 and Table 3) reflects the tendency of Cd to sorb to reducible soil phases (Ho and Evans, 2000; Száková et al., 1999). The $\%Cd_{dff\_recovery}$ in F2 corresponds well with iron concentrations

(Sterckeman et al., 2009). Both the $\%Cd_{dff\_recovery}$ in F2 and iron concentrations were about twice as high in OEN compared with in ZOFE (Table 1). Cd_{dff} partitioned into F2 is less mobilizable than it is in F1. This lower mobility is reflected in the lower $\%Cd_{dff\_recovery}$ in shoots on the OEN soil than on the ZOFE soil (Fig. 2). The reduced potential mobility of Cd_{dff} partitioned into F2 is confirmed by the isotopic mixing models, which indicate that less than 7.3% of Cd in shoots originated from F2 in both soils (Fig. 3). This finding agrees with the results of Ahnstrom and Parker (2001), which show that less than 10% of freshly applied Cd partitioned into the reducible fraction was exchangeable after two weeks of incubation. Thus, Cd_{dff} partitioned into F2 is not considered to be a significant Cd_{dff} source for wheat under oxic conditions. In contrast, Cd_{dff} partitioned into F2 is potentially mobilizable under reducing conditions (e.g., waterlogging) because of the slow dissolution of oxides (He et al., 2005).

The oxidizable F3 and the inert F4 only represented a minor share of $\%Cd_{dff\_recovery}$ in both soils. The twice as high $\%Cd_{dff\_recovery}$ in F3 in the OEN soil compared with in the ZOFE soil (Fig. 2 and Table 3) can be explained by threefold higher soil organic carbon concentrations in the OEN soil than in the ZOFE soil (Table 1) (Buekers et al., 2008; Grant and Sheppard, 2008; Smolders and Mertens, 2013). Cd_{dff} partitioned into F3 is not considered to be mobile because it is expected to be released only slowly during the decomposition of soil organic matter (Filgueiras et al., 2002; Rao et al., 2008). Moreover, the isotope mixing models revealed that there was a small contribution (<5%) of F3 to the Cd in wheat. As expected, the inert F4 had a negligible importance for the $\%Cd_{dff\_recovery}$ and as a source fraction for Cd in shoots.

5. Conclusions

This study applied a novel combination of enriched stable Cd isotope source tracing methods. Isotopic mass balances, sequential extractions, and Bayesian isotope mixing models were coupled to trace Cd_{dff} in soil-wheat systems with distinct soil properties (strongly acidic and neutral soil pH) and with distinct past mineral P applications. Our results show that:

- Soil Cd concentrations increased with increasing past mineral P fertilizer rates in the neutral but not in the strongly acidic soil. Higher soil Cd concentrations in the unfertilized treatments of the strongly acidic soil was due to the much higher biomass production on the fertilized treatment in the field experiment and thus higher Cd extraction with harvest. In the pot experiment, shoot Cd concentrations only increased in the neutral soil when past P fertilizer application rates were higher than crop P offtake.
- Only a small share (less than 2.3%) of freshly applied Cd_{dff} was taken up by the wheat plant. Over 97.7% of freshly applied Cd_{dff} remained in the soil.
- Cd_{dff} that remained in the soil was predominantly (over 95% of applied Cd_{dff}) partitioned into the acetic acid soluble (F1) and the reducible (F2) fractions. Cd_{dff} partitioned into F1 is considered easily mobilizable and potentially plant available.
- Bayesian mixing models showed that over 80% of the Cd in shoots originated from F1, thereby confirming the high potential plant availability of Cd_{dff} partitioned into F1.
- Soil pH was the determining factor for the partitioning of Cd_{dff} into F1. The role of soil pH was highlighted by a Cd_{dff} recovery of about 40% of freshly applied Cd_{dff} in F1 in the neutral soil compared to about 60% in the strongly acidic soil.
- Freshly applied Cd_{dff} remains mobilizable and potentially plant available in the subsequent crop cycle.

The enriched stable isotope labeling approach enabled a precise tracing of Cd_{dff} in the soil and in wheat. In the future, this approach can provide valuable data for risk assessments of Cd containing fertilizers that originate from mineral, recycled or organic sources. For fertilizers that are less soluble than the one used in this study (see SI-3), it would be possible to isotopically label the soil instead of the fertilizer. Stable isotopic labeling can also be used in the field by applying enriched stable isotopic labels to subplots or lysimeters to study the fate of Cd_{dff} over several harvest cycles. This study's methodological approach is also potentially suitable for tracing other heavy metals that have multiple stable isotopes.

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Author statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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